(12) EUROPEAN PATENT APPLICATION

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(54) Improving corrosion resistance of zirconium alloys.

(57) A process for improving the corrosion resistance and reducing hydrogen absorption of zirconium alloys to be used, for example, in a light water nuclear reactor environment, comprises implanting the alloy surface with chromium ions. Implantation is conducted at an incident ion energy of about 75 keV and a dose of about 7.0×10^{16} ions/cm² to 1.4×10^{17} ions/cm² until an approximate chromium surface concentration of 2 to 40 atomic percent is achieved.

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IMPROVING CORROSION RESISTANCE
OF ZIRCONIUM ALLOYS

This invention relates to processes for improving the corrosion resistance of zirconium alloys (such as, for instance, Zircaloy), which alloys may, for example, be used in light water nuclear reactor environments.

Zirconium alloys have been extensively used in nuclear reactor systems due to their optimal low neutron cross-section (low tendency to capture neutrons), generally good corrosion resistance in water and steam, and adequate strength for cladding uranium oxide fuel used in light water reactors.

Future reactor designs and utilizations are placing more emphasis on ensuring adequate corrosion resistance. Improvements in the corrosion resistance of
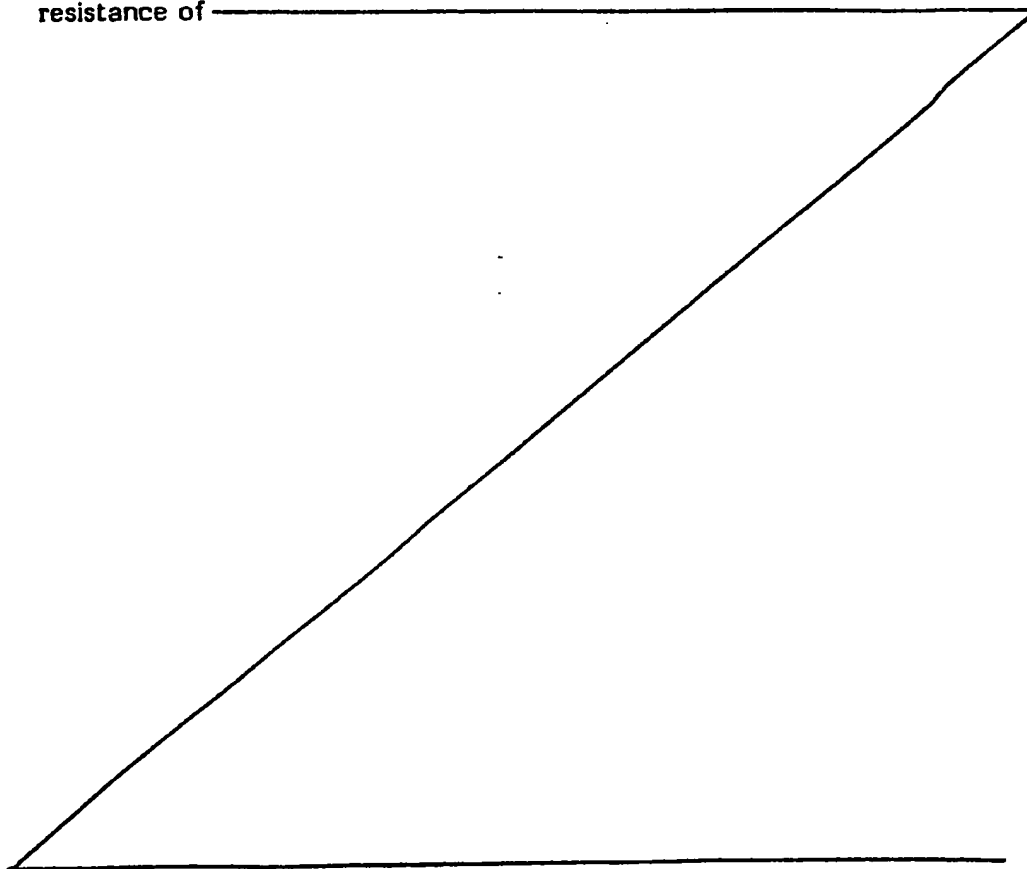
the zirconium alloy Zircaloy-4, for example, while retaining the benefits of its other favourable properties, is a highly desirable goal for advanced applications.

Zircaloy-4 is an alloy composed principally of zirconium (Zr) but also containing, on a weight percent basis, 1.20 to 1.70 % tin, 0.18 to 0.24% iron and 0.07 to 0.13% chromium.

The corrosion of Zircaloy-4 in water or steam occurs by the growth of a zirconium oxide layer produced by the reaction $Zr + 2H_2O \rightarrow ZrO_2 + 2H_2$. The growth of this layer occurs initially by either cubic or parabolic oxidation kinetics, but after a certain weight gain, the kinetics of growth are linear. The oxide film in general is quite adherent well out into the linear kinetics region. However, at a certain oxide thickness, the oxide adherency is seriously impaired and spalling or "breakaway" occurs. In nearly all present applications, the breakaway region is not reached.

During the corrosion reaction, however, hydrogen is produced. Part of this hydrogen is absorbed by the Zircaloy-4 metal while the balance is carried off in the water or steam coolant. Hydrogen absorbed by the Zircaloy-4 will eventually reach sufficient concentrations so that zirconium hydrides will form in the Zircaloy-4. The hydride formations can lead to degraded ductility and fracture toughness in the Zircaloy-4 at lower service temperature.

Improvements in the corrosion resistance can therefore occur by lowering the rate of corrosion, by eliminating the change to linear kinetics, by extending the time to film breakaway and by reducing the pick-up fraction for hydrogen in Zircaloy-4. Alloy modifications have been looked at from time to time, but the generally good corrosion behaviour and adequate strength of Zirca-

loy-2, Zircaloy-4, Zr-1Nb, Zr-2.5Nb and Ozhennite (Zr-Sn-Nb-Fe-Ni) have tended to limit any further development of commercial reactor grade alloys. However, current concerns over nodular corrosion in boiling water reactors (BWRs) and over the variable corrosion resistance at extended burnup in both BWRs and pressurized water reactors (PWRs) generated a need to look at ways to improve existing alloy grades through modified thermomechanical processing and possibly alloy changes. Alloy modifications and thermo-mechanical treatments, attempted over the years to improve the corrosion resistance of Zircaloy-4 and other zirconium alloys, in general, alter either the chemistry or the structure of the entire material section, or both. This can lead to variability in the effectiveness throughout the material and alter the other properties of the alloy in an undesirable manner.

Ion implantation is generally known as an effective technique for preparing surface alloys of controlled composition without affecting the underlying bulk structure and properties of the metal. Ion implantation is the process by which sufficiently energetic ions are propelled into the surface of a host material (metal, ceramic or plastics), sometimes referred to as a matrix, such that penetration beyond surface layers occurs. This is achieved by accelerating an ion species to energies between 3 to 500 keV with resulting target penetrations to depths of 100 to 10,000 angstroms below the surface. The ion species is accelerated in vacuum through an appropriate electric potential and electromagnetically aligned and collimated to strike the material target. At low energies, the ions essentially plate onto the material target and can subsequently be distributed into the target material through an inert ion (such as xenon) bombardment. At high energies, the ion species are driven into

the target material creating a distribution or mixing of
the implant ion with the target material.

Use of ion implantation for surface modification
of surface sensitive properties of materials by changing
5   the mechanical and chemical behaviour of the surface layers
is now the subject of growing research and application.
Numerous surface properties of materials are influenced by
surface composition. Such properties include friction,
wear, hardness, fatigue, corrosion, resistance, electro-
10   chemistry, catalysis, decorative finish, bonding, lubrica-
tion, adhesion and reflectance. Hence, ion implantation
holds promise as a technique for altering such surface
properties.

Ion implantation thus offers a method for bring-
15   ing about novel surface alloy changes without altering the
acceptable bulk mechanical properties of the existing zir-
conium alloys. Because of the potential for non-equili-
brium phase structure, alloy conditions can be created
which have never been evaluated before due to the nearer
20   chemical equilibrium imposed by traditional high tempera-
ture metal processing of zirconium alloys.

Alloy development work performed on zirconium
during the 1960's showed that a Zr-1.2%Cr - .08%Fe alloy
(Valloy) when properly processed produced an alloy super-
25   ior to the Zircaloy-2 in 400°C and 500°C steam and
.   equivalent behavior in 300°C steam. Critical to this
improved performance is the necessity to retain 0.7%
(0.4%) Cr in solution and to have an intermetallic parti-
cle size much less than 1 micrometre in size. These
30   requirements are achieved by quenching from the beta phase
and a specific fabrication schedule. Lot to lot variabi-
lity in corrosion behaviour has reportedly been the main
reason for lack of commercial acceptance of this alloy.

In accordance with the present invention, a process of ion implantation is used to add chromium elements to Zircaloy-4 or other zirconium based alloys to alter the surface composition and the crystalline structure of the alloy's surface.

5   According to one aspect of the invention there is provided a process for improving the corrosion resistance and reducing hydrogen absorption of a zirconium alloy, the process comprising implanting chromium ions into the surface of the zirconium alloy at an incident ion energy of about 75 keV and a dose of about 7.0×10^{16} ions/cm^2 to 1.4×10^{17} ions/cm^2 until an

10   approximate chromium surface concentration of 2 to 40 atomic percent is achieved.

According to another aspect of the invention there is provided a process in which chromium ions are directly implanted into Zircaloy-4 to create a chromium concentration layer of less than 2000 angstroms deep.

15   The desired surface concentrations are 2, 20 and 40 atomic percent. These are 1.4×10^{17} Cr ions/cm^2. The Cr ion energy for implantation is 75 keV with a beam current of 1.2 mA. The implanted speciments were either tested in the as-implanted condition or given a 510°C (950°F) stress relief anneal for 2 hours.

20   Through the use of implantation of chromium, an improved corrosion resistant layer is imparted to the Zircaloy-4 and hydrogen absorption is reduced. Because of the shallowness of this modified layer, none of the bulk properties of the Zircaloy-4 will be altered. The nature of the alloying created by the ion implantation cannot be created by traditional melting,

25   hot working and heat treatment.

The invention will now be further described, by way of illustrative and non-limiting example, with reference to the accompanying drawings, in which:

Figure 1 is a graph which schematically illustrates weight gain or

30   growth of an oxidation layer of a Zircaloy-4 material as a function of time before and after a transition to linear growth;

Figures 2 to 4 graphically illustrate chromium concentration as a function of depth in Zircaloy-4 specimens which have been treated in accordance with processes embodying the invention; and

35   Figures 5 to 7 graphically illustrate corrosion weight gain of Zircaloy-4 materials which were and were not treated by processes

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embodying the invention.

The present invention will now be illustrated by reference to the following specific example, which is presented for the purpose of illustration only. The present invention is not intended to be limited thereto.

5   EXAMPLE

The surfaces of specimens or coupons composed of a zirconium alloy (Zircaloy-4 wrought flat plate 28.575 mm X 22.225 mm X 4.7625 mm (1.125 inches X 0.875 inches X 0.1875 inches)) were directly bombarded with

10   chromium ion doses of 7×10^{15}, 7×10^{16}, and $1/4 \times 10^{17}$ chromium ions/cm^2 at 75 keV, to obtain surface concentrations of 2, 20 and 40 atomic percent.

The flat specimens were mechanically mounted using set screws in specimen hanger holes on metal discs 101.6 mm (4 inches) in diameter which

15   rotated under the specific ion beam. After the desired doses were achieved on one side, the specimens were removed and turned over to implant the opposite face of the specimens. Beam incidence was normal in these implants. The side edges of the specimens and the hole surfaces were not implanted since they were parallel to the implant beam. The implantation

20   was performed in less than 10^{-6} torr Ar. The specimens could be viewed during implantation and a pale blue-violet glow emanated from the surfaces during implantation. Specimen heating occurs in an estimated temperature range of 93 to 204°C (200 to 400°F).

After implantation, a number of specimens were subjected to vacuum

25   stress relief annealing at 510°C (950°F) for two hours. Half the specimens for each implant condition were tested as implanted, the other half were tested after being stress-relief annealed. Several specimens were not implanted but kept as control specimens. Half of the unimplanted control specimens were also given the stress relief anneal treatment at the same

30   time with the selected implant specimens.

The calculated ion distributions as a function of depth from the surface are shown in Figures 2, 3 and 4. It will be understood that, as used in Figures 2 to 4, the term "sputtered surface" is used to refer to the final surface created by sputtering Zr and Cr atoms from the surface by Cr ions

35   during implantation. At a chromium dose of 7×10^{15}, the calculated

surface concentration is about 1% with a maximum concentration of about 3% at 400 angstroms. The total depth of chromium penetration was approximately 1,000 angstroms. At doses of 7×10^{16} and 1.4×10^{17}, the estimated surface concentration was 24% and 50%, respectively. The as-sputtered surface had the maximum concentration in the distribution. The depth of chromium penetration was estimated to be 1,300 angstroms in both the intermediate and high chromium doses.

Colour changes in some of the surfaces of chromium implanted surfaces were observed. At the low chromium dose of 7×10^{15} no discolouration was observed. After 7×10^{16}, however, colours ranging from dark gold, purple, dark blue, steel gray and straw were observed. At 1.4×10^{17} ion/cm^2, specimens which previously had gold, purple, and blue variations on their surface became uniformly gold in colour. The subsequent two hour, 510°C (950°F) vacuum stress relief on half of the specimens eliminated any trace of colouration.

Weights and dimensions of the specimens were measured before and after implantation. The post-implantation dimensions were used for subsequent weight gain per unit surface area measurement calculations.

Corrosion effects were determined by the technique of weight gain determination. Corrosion testing of the implanted and control specimens was performed in $399^\circ \pm 2.78^\circ$C ($750^\circ \pm 5^\circ$F) steam at 10.34 ± 0.69MPa (1500 ± 100 lbf/in^2). The specimens were reweighed and alcohol cleaned prior to the start of testing. The mass of each specimen is known within ± 0.05 mg, which, when combined with the surface area measurement accuracy, allows the weight gain to be determined within ± 0.25 mg/dm^2. The specimens were periodically reweighed. Weight gains per dm^2 were based on untested surface area dimensions.

The testing schedule was designed to provide sufficient data points in the early cubic kinetics region out to about 30 to 35 days behaviour as well as to provide key comparisons with normal Zircaloy-4 behaviour at 3, 7, and 14 days. The "normal" corrosion behaviour in the cubic or pre-transition range, as shown by Figure 1, was modelled. The transition from cubic to linear kinetics occurs at a weight gain of approximately 33 mg/dm^2 which takes about 36 days to reach in 399°C (750°C) steam for normal Zircaloy-4. The specific weight gains for each specimen were determined as a function of exposure time and are illustrated by Figures 5, 6 and 7.

Figures 5, 6 and 7 show specific weight gains as a function of exposure time for the three dose levels of chromium. The control specimen data is plotted with the implanted specimens on each graph.

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For each of Figures 5, 6 and 7, actual weight gain values of the implanted specimens are adjusted by assuming areas not implanted to have the same weight gain as the appropriate control.

Figure 6 shows that for pre-transition corrosion (i.e. less than 36 days) the specimens implanted with a dose of 7×10^{16} chromium ions/cm^2 have the lowest weight gains of any tested. The as-implanted specimens at

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this dose exhibit the least specific weight gain of 23.30 mg/dm^2 at 33.95 days of exposure compared to 39.45 mg/dm^2 for the as-received control coupons. The stress relief annealed chromium implanted specimens at this dose had 31.20 mg/dm^2 weight gain compared to 43.77 mg/dm^2 for the stress relief annealed control coupons.

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Specimens with a 1.4×10^{17} chromium ions/cm^2 dose also show some reduction in specific weight gain compared to the control specimens in Figure 7. Again, the as-implanted specimens show somewhat lower weight gains of 31.60 mg/dm^2 than their stress-relief annealed counterparts which had 36.3 mg/dm^2.

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At a dose of 7×10^{15} Cr ions/cm^2, the implanted specimens showed a marginal reduction in weight gain in Figure 5 compared to the control specimens. The as-implanted specimens were at 33.65 mg/dm^2 compared to the 39.45 mg/dm^2 for the as-received control specimens. The stress relieved counterparts were similar to the control specimen behaviour with

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39.20 mg/dm^2 compared to 43.77 mg/dm^2 for the stress relieved control specimens.

In the post-transition linear kinetics region, the chromium implanted specimens generally showed continued lower weight gains compared to the control specimens. This occurs not only because of the lower weight gain coming off the pretransition region, but also because the slope or rate of

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weight gain for the chromium implanted specimens in post-transition is smaller. Specimens with a 7×10^{16} chromium ion/cm^2 dose continue to show the lowest weight gains, followed by the as-implanted 7×10^{15} and 1.4×10^{17} chromium ions/cm^2 dose specimens. At 7×10^{16} chromium

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ions/cm^2 the slope, or corrosion rate, is 0.49 (mg/dm^2)/day for the as-implanted specimens and 0.46 (mg/dm^2)/day for the stress relieved

specimens. This compares to 0.58 and 0.61 $(mg/dm^2)/day$ for the as-received and stress relieved control specimens, respectively. Rates of 0.46 and 0.48 $(mg/dm^2)/day$ were measured for the as-implanted specimens at 7×10^{15} and 1.4×10^{17} chromium ions/cm^2, respectively. The stress relieved specimens at 7×10^{15} and 1.4×10^{17} chromium ions/cm^2 show no improvement over the controls.

The hydrogen content of the chromium implant specimens was lower on the average than the control specimens. As shown in the Table appearing hereinbelow, after 105 days the chromium implanted specimens had an average of 27.0 ± 6.1 ppm hydrogen as compared to an average of 38.0 ± 5.0 ppm hydrogen for the control specimens. To normalize out the effect of different amounts of corrosion or weight gain, the ratio of hydrogen content to weight gain was taken. The chromium implant specimens have a lower pick-up of hydrogen per unit weight gain than the control specimens. The specimens implanted with chromium had an average 0.267 ± 0.062 ppm hydrogen per unit weight gain compared to 0.353 ± 0.066 ppm hydrogen per unit weight gain for the control specimens.
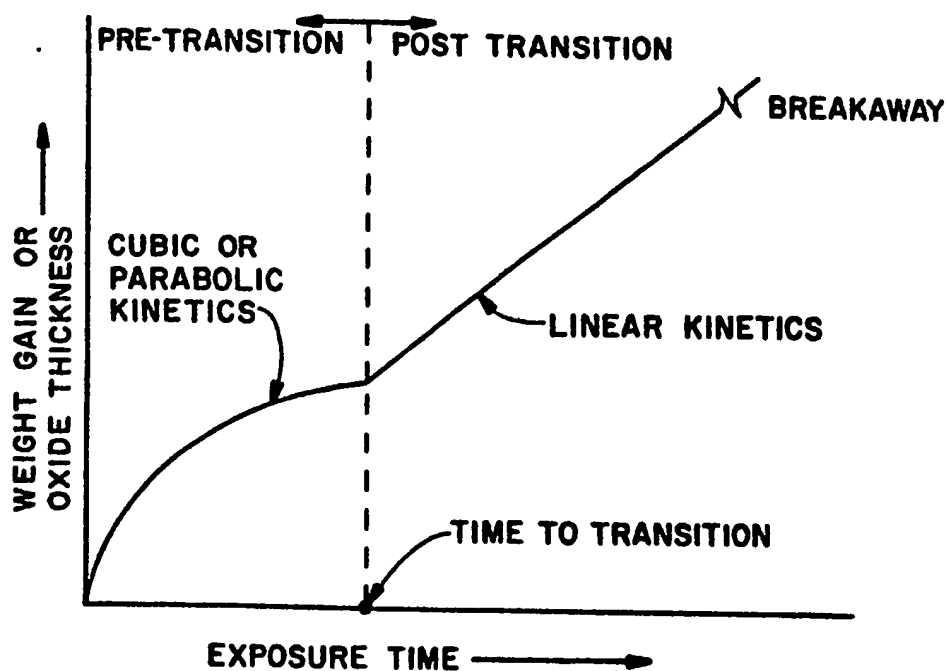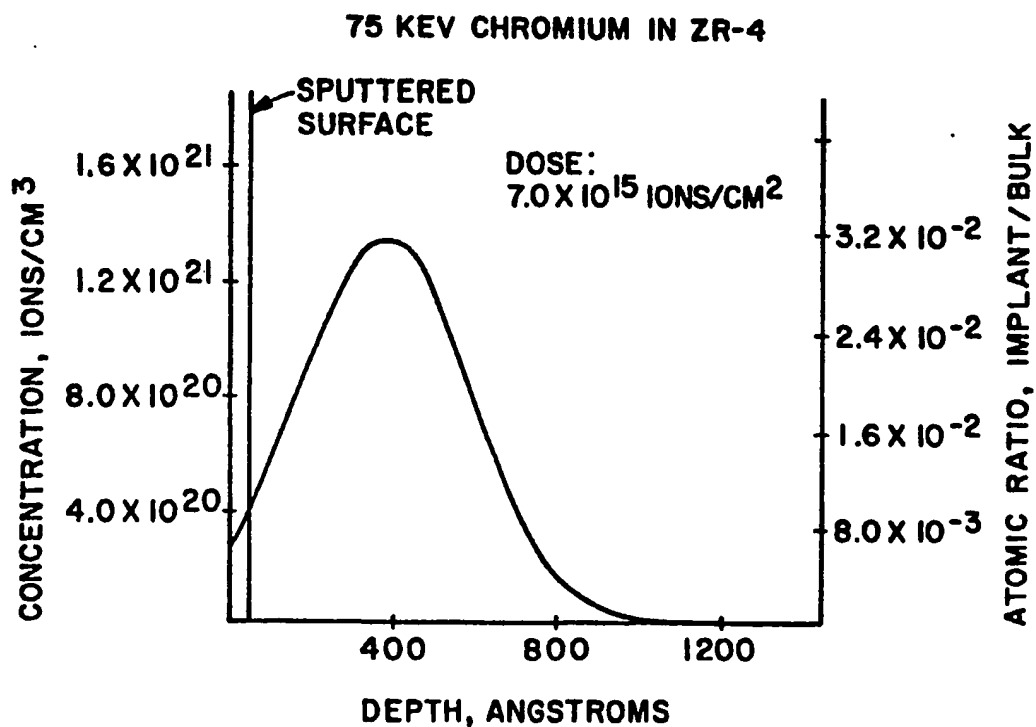
In summary, the best performing chromium implant in pre-transition was the as-implanted 7×10^{16} ion/cm^2 dose specimen which had a 41% lower weight gain than the as-received control specimens. In post-transition, reductions in corrosion rate of 16% to 25% were achieved over the various combinations of ion dose and anneal. Only the stress relieved specimens at 7×10^{15} and 1.4×10^{17} ions/cm^2 showed no reduction in corrosion rate. As a group, the chromium implants showed a 24% reduction in hydrogen pickup per unit weight gain.
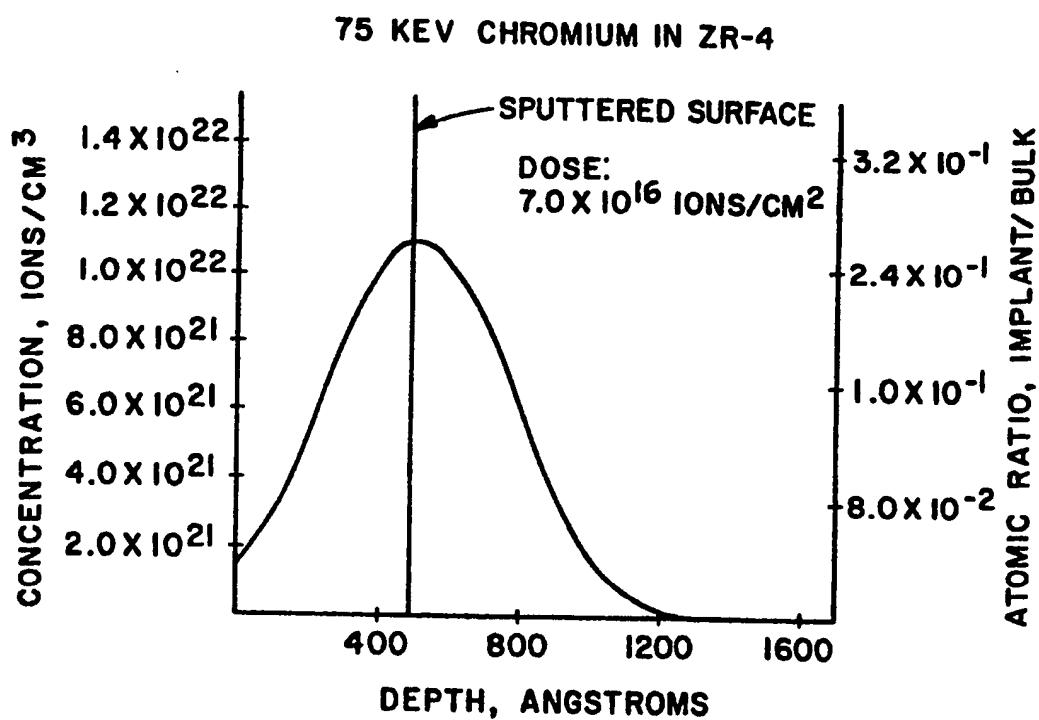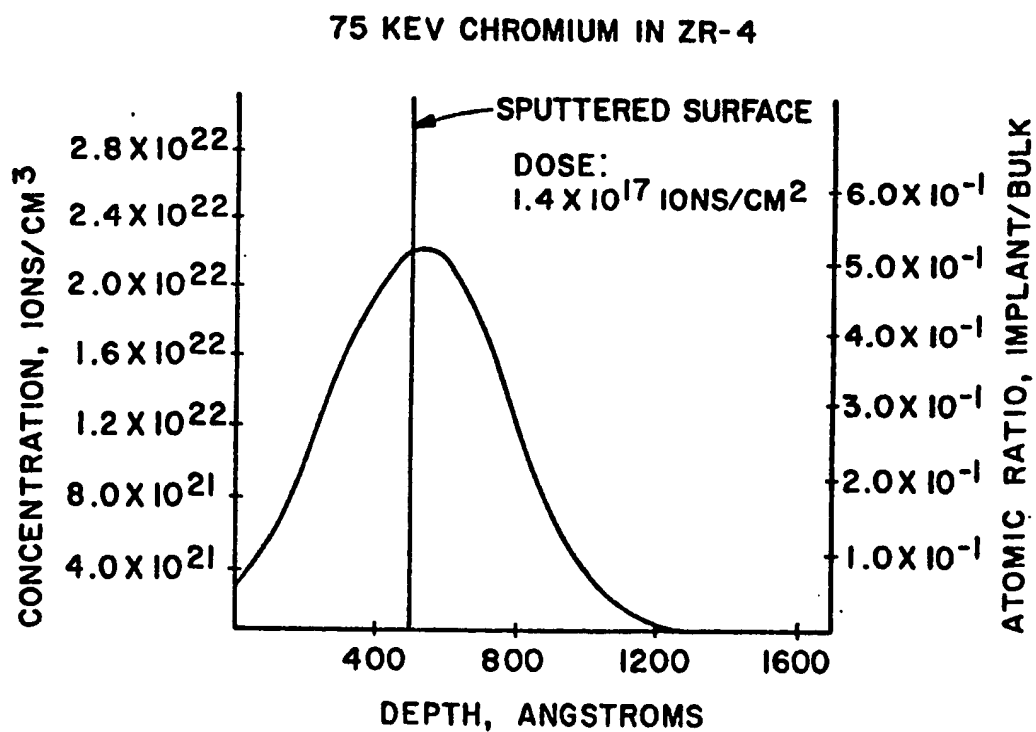
TABLE

Hydrogen Content After 105 Days

Specimen Number	Ion	Dose, ions/cm^2	Condition	Hydrogen Content ppm	Hydrogen Pick-up/ Specific Weight Gain, ppm H/(mg/dm^2)
1	Cr	7×10^{15}	As-implanted	27	0.28
2	Cr	7×10^{15}	Stress relieved	29	0.24
3	Cr	7×10^{16}	As-implanted	23	0.25
4	Cr	7×10^{16}	Stress relieved	18	0.17
5	Cr	1.4×10^{17}	As-implanted	29	0.31
6	Cr	1.4×10^{17}	Stress relieved	36	0.35
			Average Value	27.0 ± 6.1	0.267 ± 0.062
7	Control	None	As-received	43	0.44
8	Control	None	As-received	35	0.32
9	Control	None	As-received	36	0.34
10	Control	None	Stress relieved	45	0.43
11	Control	None	Stress relieved	37	0.31
12	Control	None	Stress relieved	32	0.28
			Average Value	37.0 ± 5.0	0.353 ± 0.066

CLAIMS

1. A process for improving the corrosion resistance and reducing hydrogen absorption of a zirconium alloy, the process comprising implanting chromium ions into the surface of the zirconium alloy at an incident ion energy of about 75 keV and a dose of about 7.0×10^{16} ions/cm^2 to 1.4×10^{17} ions/cm^2 until an approximate chromium surface concentration of 2 to 40 atomic percent is achieved.

2. A process according to claim 1, comprising annealing the implanted zirconium alloy.

3. A process according to claim 1 or claim 2, wherein the alloy is Zircaloy-4.

PRE-TRANSITION | POST TRANSITION

BREAKAWAY

WEIGHT GAIN OR OXIDE THICKNESS

CUBIC OR PARABOLIC KINETICS

LINEAR KINETICS

TIME TO TRANSITION

EXPOSURE TIME

FIG. 1

75 KEV CHROMIUM IN ZR-4

SPUTTERED SURFACE

DOSE: 7.0×10^{15} IONS/CM^2

CONCENTRATION, IONS/CM^3

1.6×10^{21}

1.2×10^{21}

8.0×10^{20}

4.0×10^{20}

ATOMIC RATIO, IMPLANT/BULK

3.2×10^{-2}

2.4×10^{-2}

1.6×10^{-2}

8.0×10^{-3}

400   800   1200

DEPTH, ANGSTROMS

FIG. 2

75 KEV CHROMIUM IN ZR-4

FIG. 3

75 KEV CHROMIUM IN ZR-4

FIG. 4

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ION IMPLANTATION
CHROMIUM
7×10^{15} IONS/CM^2
EXPOSED SURFACES ONLY

WEIGHT GAIN MG/DM^2

—————— CONTROL
— — — CONTROL W/S.R. ANNEAL
—·——·—IMPLANTED
—··—··—IMPLANTED W/S.R. ANNEAL

CORROSION DAYS

FIG. 5

ION IMPLANTATION
CHROMIUM
7×10^{16} IONS/CM^2
EXPOSED SURFACES ONLY

WEIGHT GAIN MG/DM^2

—————— CONTROL
— — — CONTROL W/S.R. ANNEAL
—·——·— IMPLANTED
—··—··— IMPLANTED W/S.R. ANNEAL

CORROSION DAYS

FIG. 6

ION IMPLANTATION
CHROMIUM
1.4×10^{17} IONS/CM^2
EXPOSED SURFACES ONLY
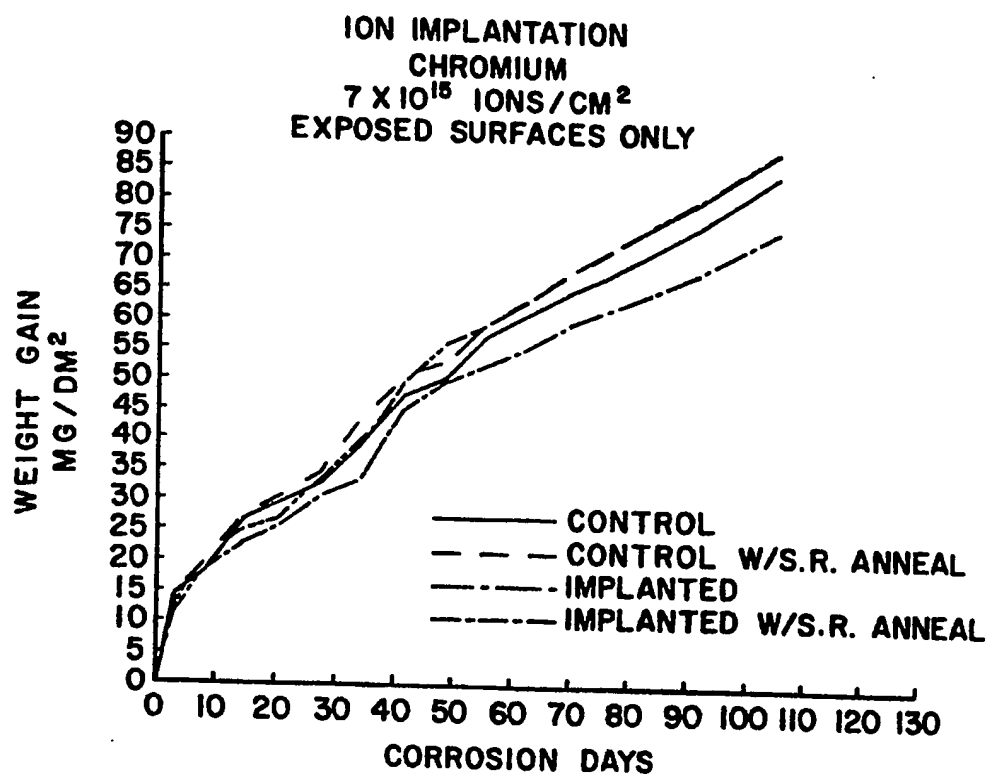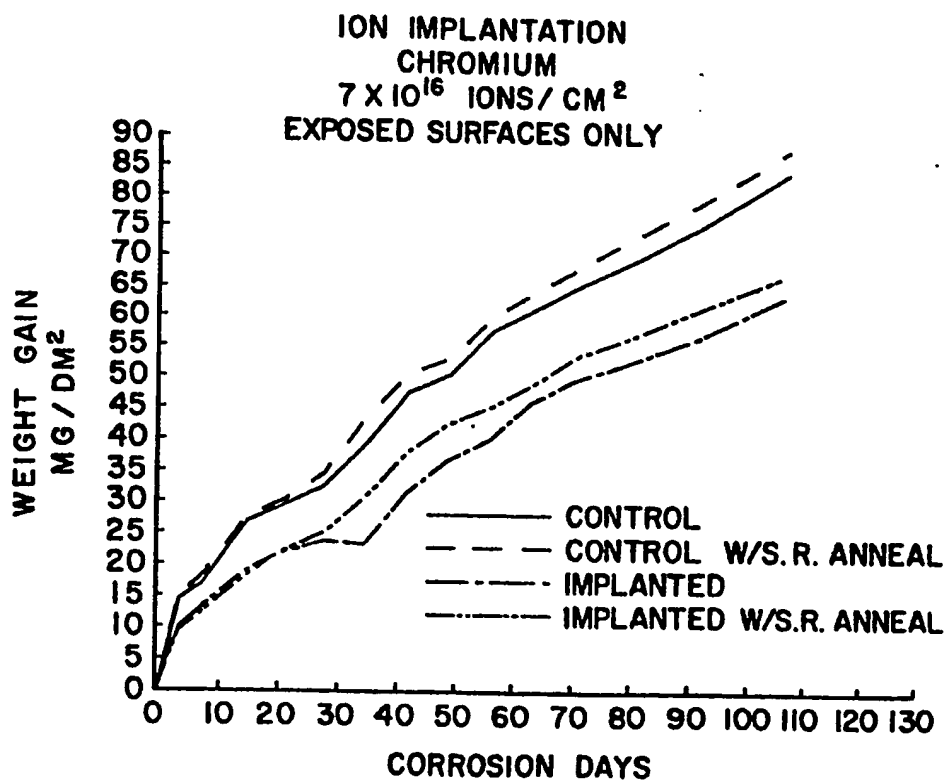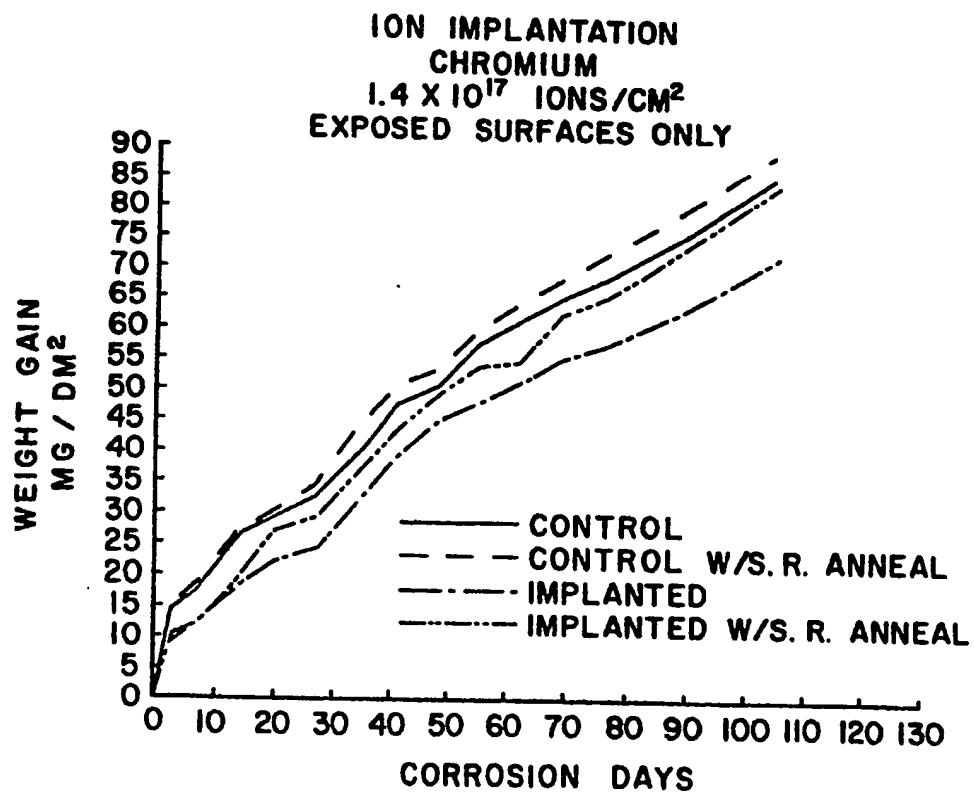

FIG. 7

European Patent Office

EUROPEAN SEARCH REPORT

Application number

	DOCUMENTS CONSIDERED TO BE RELEVANT		EP 87300952.6

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	EP - A1 - O 166 349 (SUMITOMO ELECTRIC INDUSTRIES LIMITED) * Claims, especially 3 * --	1	C 23 C 14/48 C 22 C 16/00 C 23 F 11/00
Y	DE - A - 1 483 211 (EUROPÄISCHE ATOMGEMEINSCHAFT EURATOM) * Claims * --	1	
A	DE - A - 2 409 461 (COMMISSARIAT A L'ENERGIE ATOMIQUE) * Claims * --	1	
A	US - A - 4 279 667 (T.R.ANTHONY et al.) * Claims * --	1,3	
A	US - A - 4 046 659 (R.L.CORMIA et al.) * Claims * ----	1	**TECHNICAL FIELDS SEARCHED (Int. Cl.4)** C 23 C C 22 C C 23 F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	23-04-1987	SLAMA

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document